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14. ABSTRACT

This is a presentation for the American Chemical Society's Fall National Meeting, about Fluoroalkyl Polyhedral Oligomeric Silsesquioxane (F-POSS) Based Monomers and Polymers.

15. SUBJECT TERMS

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FLUOROALKYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS) BASED MONOMERS AND POLYMERS

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Propulsion Directorate

Edwards Air Force Base, CA

Denver, CA

ACS Meeting 2011

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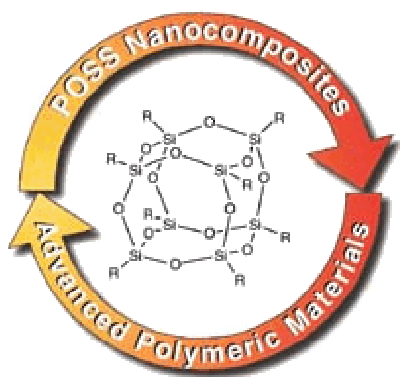

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Dr. Andy Guenthner
Dana Pinson

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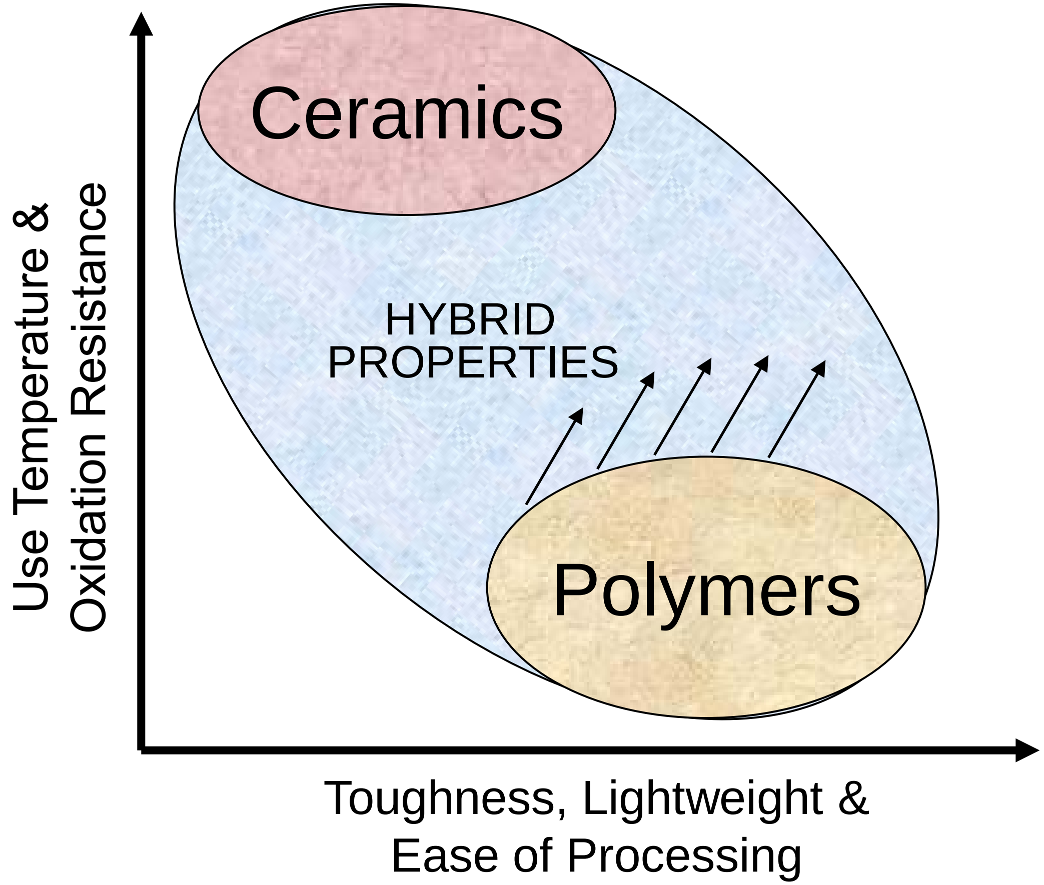
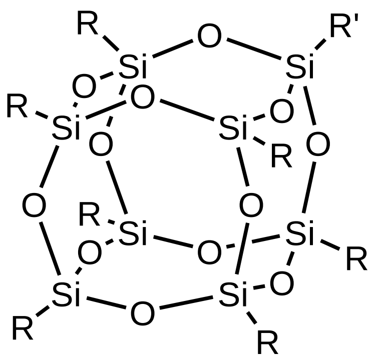
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

Hybrid Inorganic/Organic Polymers





POSS $(RSiO_{1.5})_n$

- Organic-inorganic framework
- Well-defined, 3-D nanostructure
- Can carry functional groups
- Thermally and chemically robust
- Used in thermoset and thermoplastic polymers, temperature nanocomposites, coatings, surface modifiers, and many other applications

Inorganic Si-O core

Organic peripheral

~0.5 nm Si to Si
0.5-1.5 nm particles

Cordes, D. B.; Lickiss, P. D.; Rataboul, F. *Chem. Rev.* ***2010****, 110, 2081.*
Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* ***2004****, 8, 21.*

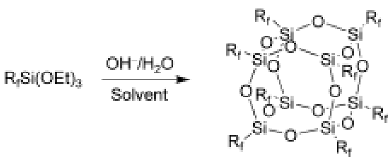
Fluorinated polyhedral oligomeric silsesquioxane (F-POSS)

F-POSS, a subclass of POSS which consists of a silicon-oxide core [$SiO_{1.5}$] with a periphery of long-chain fluorinated alkyl groups.

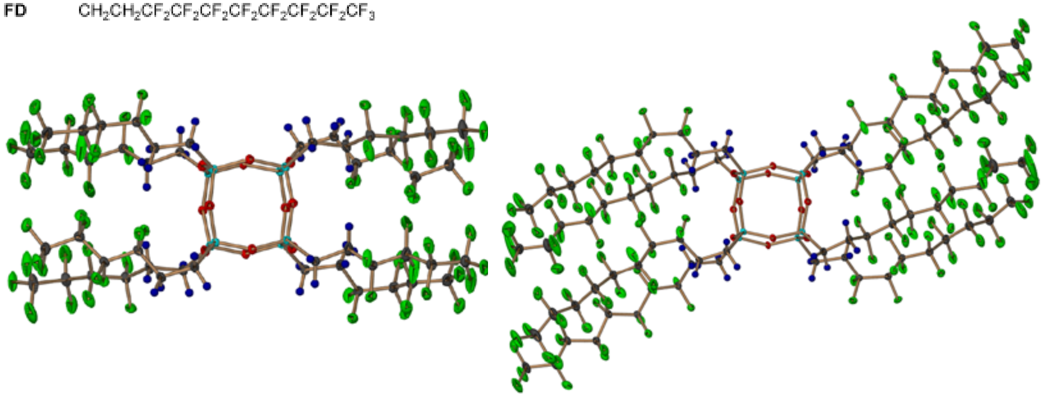
F-POSS possesses one of the lowest surface energies leading to the creation of superhydrophobic and oleophobic surfaces.

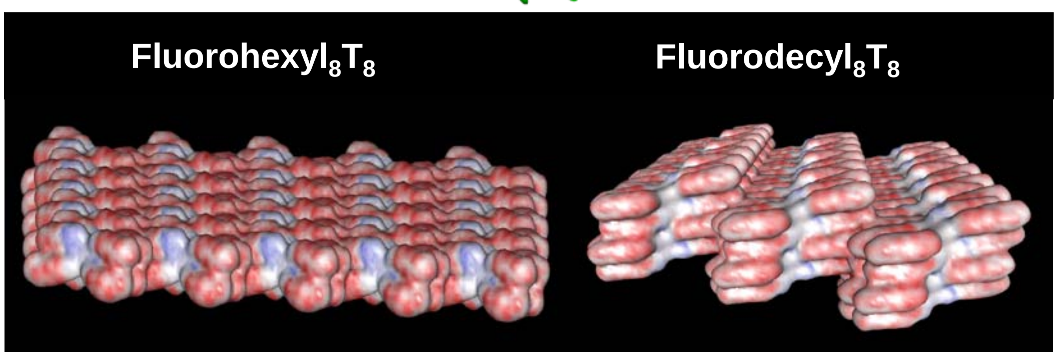
(a) Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D., *Angew. Chem., Int. Ed.* **2008,** *47*, 4137-4140; (b) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W., Jr., *Macromolecules* **2007,** *40*, 9517-9522; (c) Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M., *Chem. Commun.* **2007**, 4992-4994. (d) Choi, W.; Tuteja, A.; Chhatre, S.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H., *Adv. Mater.* **2009,** *21*, 2190-2195; (e) Tuteja, A.; Choi, W.; Mabry, J. M.; McKinely, G. H.; Cohen, R. E., *Proc. Natl. Acad. Sci. U. S. A.* **2008,** *105*, 18200-18205,; (c) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E., *Science* **2007,** *318*, 1618-1622; (f) Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E., *ACS Appl. Mater. Interfaces* **2010,** *2*, 3544-3554.

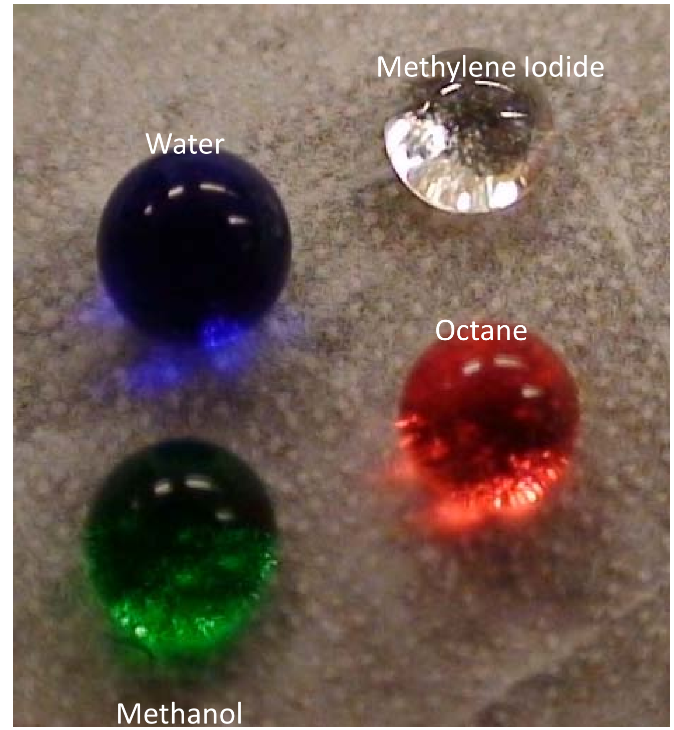
Fluorinated Polyhedral Oligomeric Silsesquioxane (F-POSS)



FH $R_f = CH_2CH_2CF_2CF_2CF_2CF_3$
FO $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_3$
FD $CH_2CH_2CF_2CF_2CF_2CF_2CF_2CF_2CF_2CF_3$







PMMA + 44 wt% POSS

electrospun coating (beads on a string) morphology

Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* ***2008,*** *47, 4137.* (left)
Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* ***2007****, 318, 1618.* (right)

Functional F-POSS

- Close-caged structures are accessible and have proven versatile in polymer composites
  - Limitations
    - Solubility, mechanical robustness (surface abrasion), no sites for functionality
- Open-caged structures would allow for functionalization of F-POSS
  - Open door for use a *building block* material for *low surface energy materials*
- Applications
  - Mechanical robust superhydrophobic/oleophobic/omniphobic surfaces
    - Via covalently attached F-POSS to substrate (surface, nanoparticle, polymer matrix)
  - Effects on polymer composite properties
    - Wetting, phase behavior, solubility, etc….

Methods to Produce Incompletely Condensed Silsesquioxanes

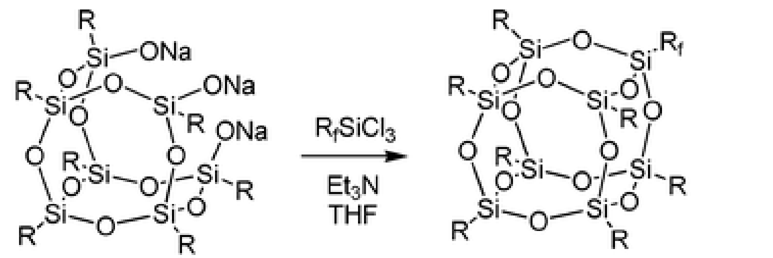
- Bottom-up approach
  - Acid or base mediated from $RSiCl_3$ or $RSi(OR)_3$
  - Condensation reaction
  - Balance of stoichiometry, temperature, reaction time, patience, and luck
  - Stopping POSS synthesis early, before cage fully condenses
  - More common approach
- Top-down Approach
  - Strong acid or base mediated
  - Starting from a POSS cage
  - Conversion of Si-O-Si bonds to Si-O $^{(-)}$ C$^{(+)}$ or Si-OH bonds
  - Opening up POSS cage

Which method can be applied to F-POSS?

Feher, F. J.; Terroba, R.; Ziller, J. W. *Chemical Communications* ***1999***, 2309. Feher, F. J.; Newman D.A;. Walzer, J.M., *J. Am. Chem. Soc.,* **1989**, 111, 1741. Feher, F. J.; Soulivong, D.; Nguyen, F.; Ziller, J. W. *Angew.Chem. Inter. Ed.****1998***, *37,* 2663. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998***, 1279.

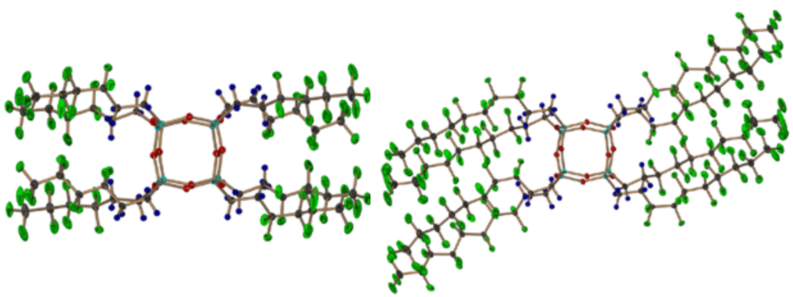
Trifluoropropyl Example

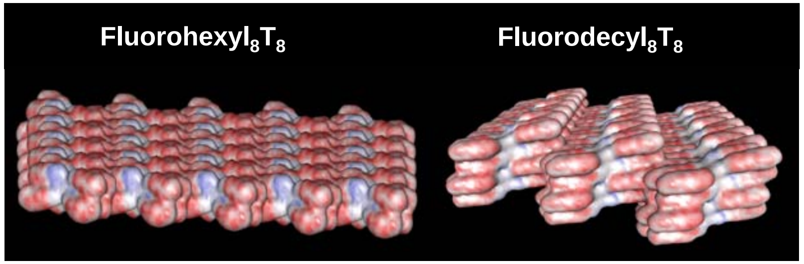
- Small chain F-POSS (propyl) have been developed and studied
- Demonstrate the robustness of an incompletely condensed silsesquioxane to functionalization



1 $R = CH_2CH_2CF_3$

2 $R_f = CH_2CH_2CF_3$
3 $CH_2CH_2(CF_2)_5CF_3$
4 $CH_2CH_2(CF_2)_7CF_3$
5 $CH_2CH_2(CF_2)_9CF_3$
6 $CH_2CH_2CH(CF_3)_2$
7 $CH_2CH_2CH_2OCF(CF_3)_2$
8 CH_3
9 $CH_2CH_2C_6H_5$





Iacono, S. T.; Vij, A.; Grabow, W.; Smith, D. W., Jr.; Mabry, J. M. *Chem. Commun.* **2007**, *4992.* Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, b. D. *Angew. Chem., Int. Ed.* **2008**, *47, 4137.*

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Synthesis of F-POSS-$(OH)_3$

R = $CH_2CH_2(CF_2)_nCF_3$

- Synthesis discussed in patents*
- Does not work for long-chain F-POSS
- Works for trifluoropropyl groups
- Solubility is critical in this reaction
- Fluorinated compounds not miscible in most organics once condensation begins to occur
- Tried under various conditions
  - Solvent, temperature, reaction time, base

- Open cages lead to functional POSS structures
- Reactions are simple
- High yields typically reported

*Yamashita, Y.; Hayashi, K.; Ishihara, M.; (Mitsubishi Materials Corp., Japan; Dai Nippon Toryo Co., Ltd.). Application: JP, 2000; pp 12 pp. Yamashita, Y.; Hayashi, K.; Ishihara, M.; (Mitsubishi Materials Corp., Japan; Dai Nippon Toryo Co., Ltd.). Application: JPJP, 2000; pp 9 pp.

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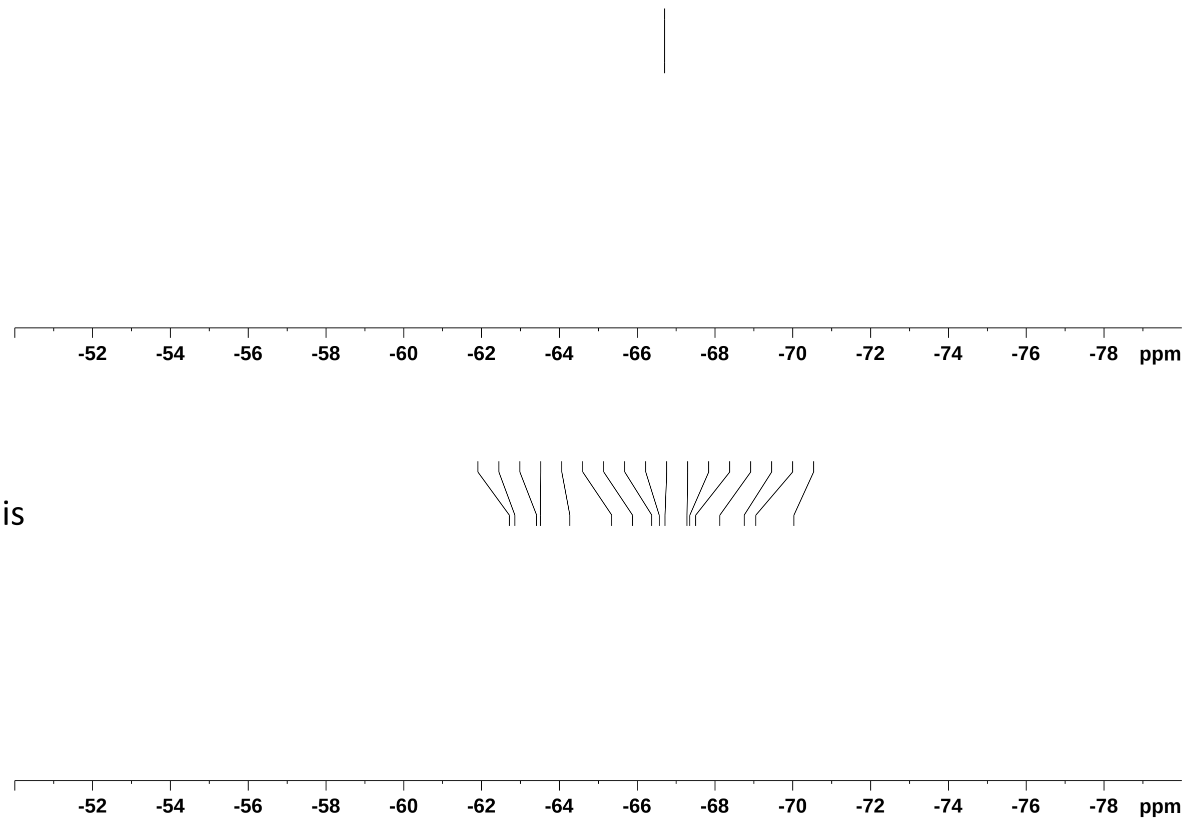
Initial Reactions with Triflic Acid

- Fluorodecyl T_8
- Reacted with triflic acid to open cage structure
- Structures analyzed with ^{29}Si NMR
- Equivalents of triflic acid to POSS cage is important to success of reaction
- Disappointing results

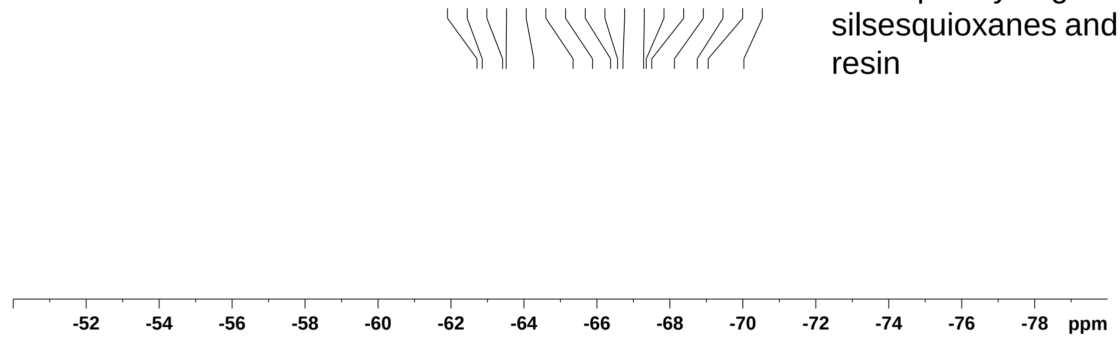


^{29}Si NMR taken in fluorinated solvent

. Feher, F. J.; Soulivong, D.; Nguyen, F. *Chem. Commun.* ***1998,*** 1279.

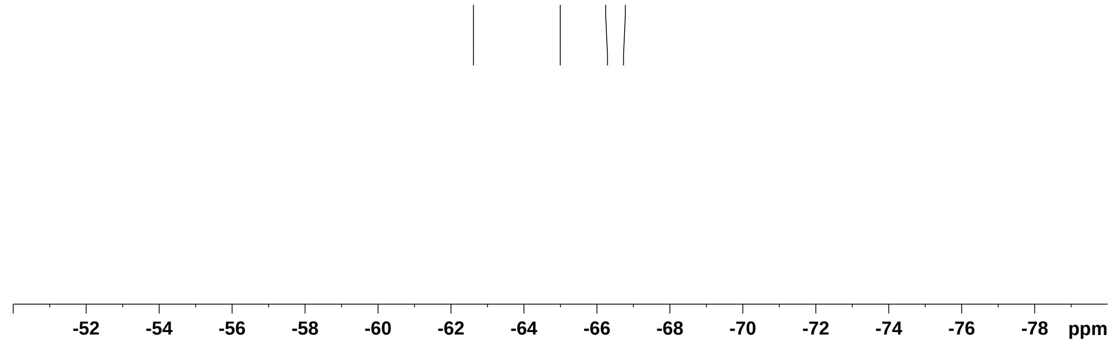
Synthesis of F-POSS-$(OTf)_2$

Mixture of unknown incompletely caged silsesquioxanes and resin



R = $CH_2CH_2(CF_2)_7CF_3$

- After a little bit of refining
- An open cage structure is partially visible
- Starting material is still present
- Reaction not very clean
- Si ratio (1:1:2)

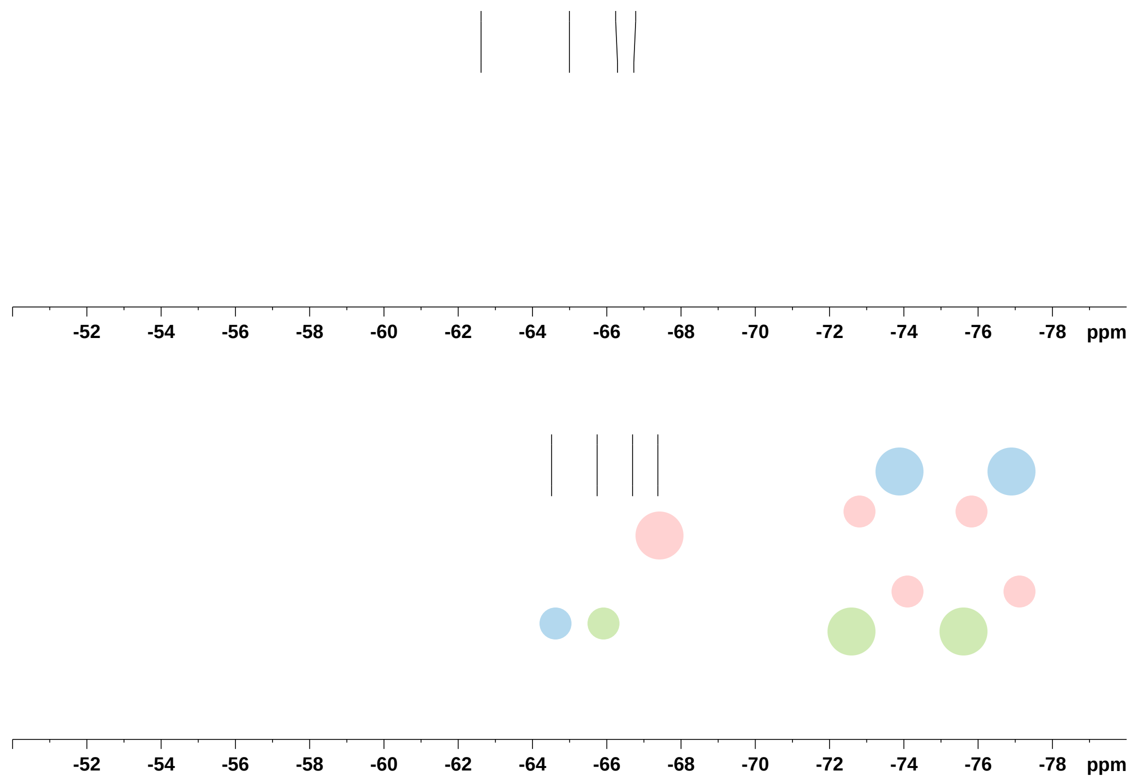


^{29}Si NMR taken in fluorinated solvent

Synthesis of F-POSS-SO_2

$R = CH_2CH_2(CF_2)_7CF_3$

- Bridge sulfate cleans up reaction
- Structure significantly more stable then then F-POSS-$(OTf)_2$, however still difficult to isolate
- Removal of starting material extremely difficult
- Si ratio (1:1:2)

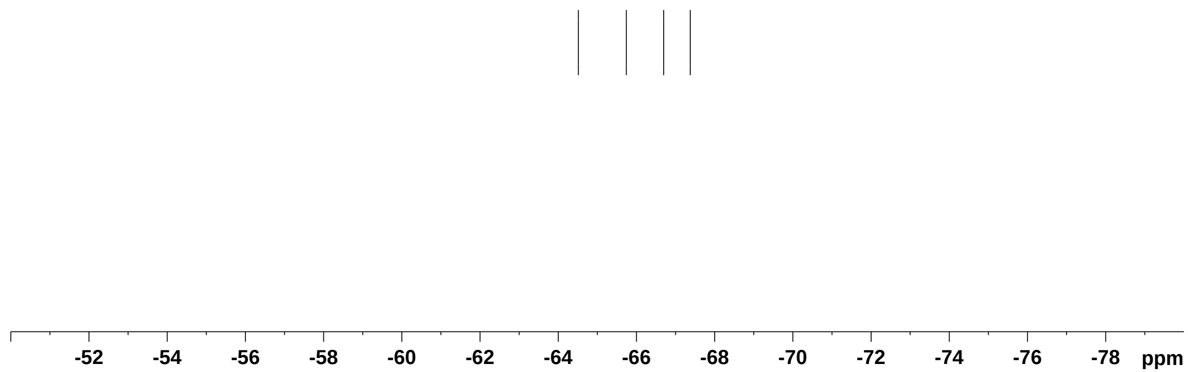


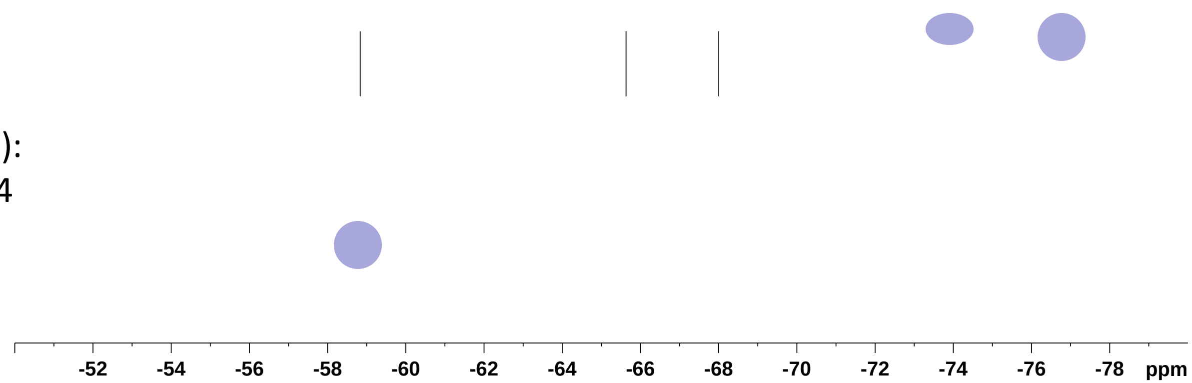
^{29}Si NMR taken in fluorinated solvent

Synthesis of F-POSS-$(OH)_2$

R = $CH_2CH_2(CF_2)_7CF_3$

- Acidic conditions are used to remove the bridge sulfate complex
- Silanol peak at -58.8 ppm
- F-POSS-$(OH)_2$ is more stable than both F-POSS-$(OTf)_2$ and F-POSS-SO_2
- Anal. Calcd. for $C_{80}H_{34}F_{136}O_{13}Si_8$ (found): C, 23.94 (23.99), H, 0.85 (0.75), F, 64.44 (64.72)
- Dehydration of disilanol leads to T_8 formation
- Si ratio (1:1:2)



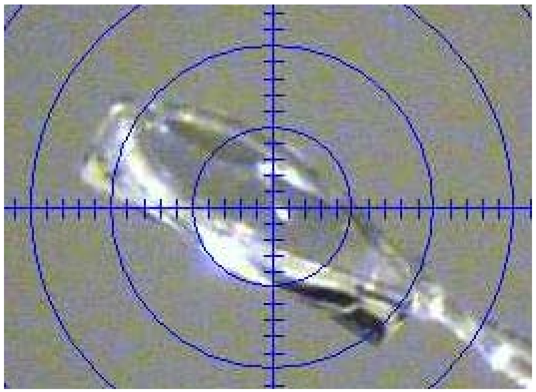


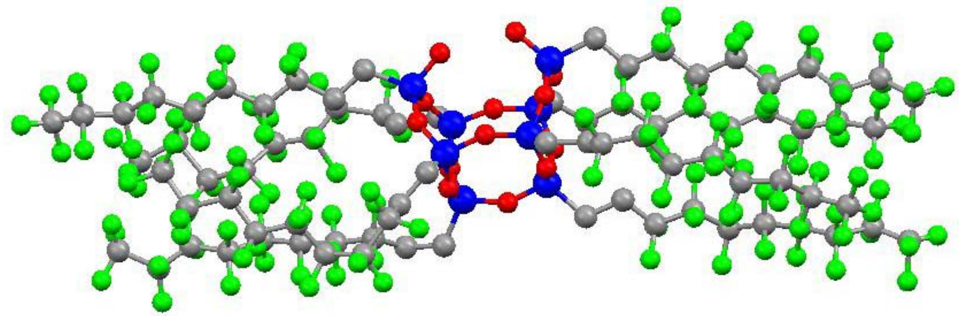
^{29}Si NMR taken in fluorinated solvent

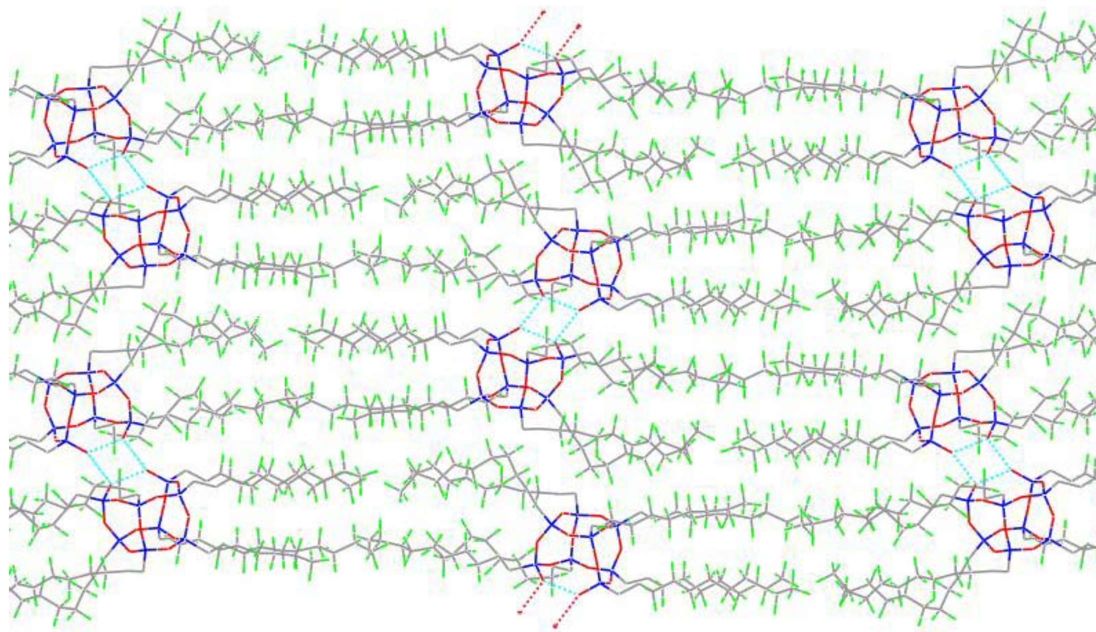
Overall Synthesis

- Isolated yield for F-POSS-(Si(OH)$_2$) is ~40-52% over the three step reaction process
- Reaction Intermediates difficult to isolate (work in progress)
- scalable
- Major side product is unreacted starting material
  - Typically this is completely recovered at the final step and recycled, starting the process all over again

X-Ray Crystal Structure of Disilanol







- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- M_r=,monoclinic, space group P2(1)/c , a=11.84(10) Å, b=57.11(6) Å, c=19.06(2) Å, α= 90.00°, β=92.21(10) °, γ=90.00 °, V= 12878(2) Å^3

Edge Capping Reactions

R = $CH_2CH_2(CF_2)_7CF_3$
R_1 = CH_3
R_2 = $CH_2CH_2CH_2OC(O)CHCH_2$

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes

Macromer/RBM = 4178 g/mol

Edge Capping Reactions

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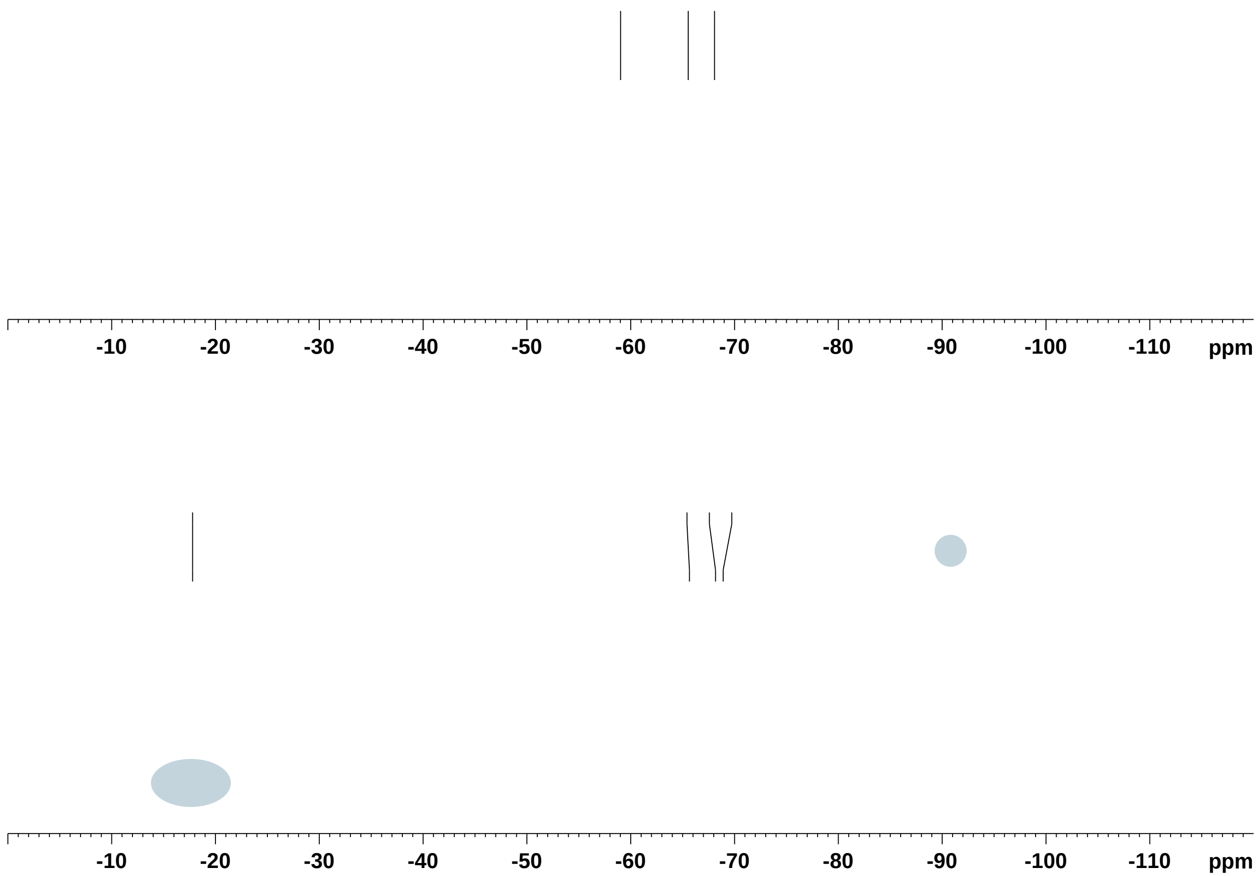
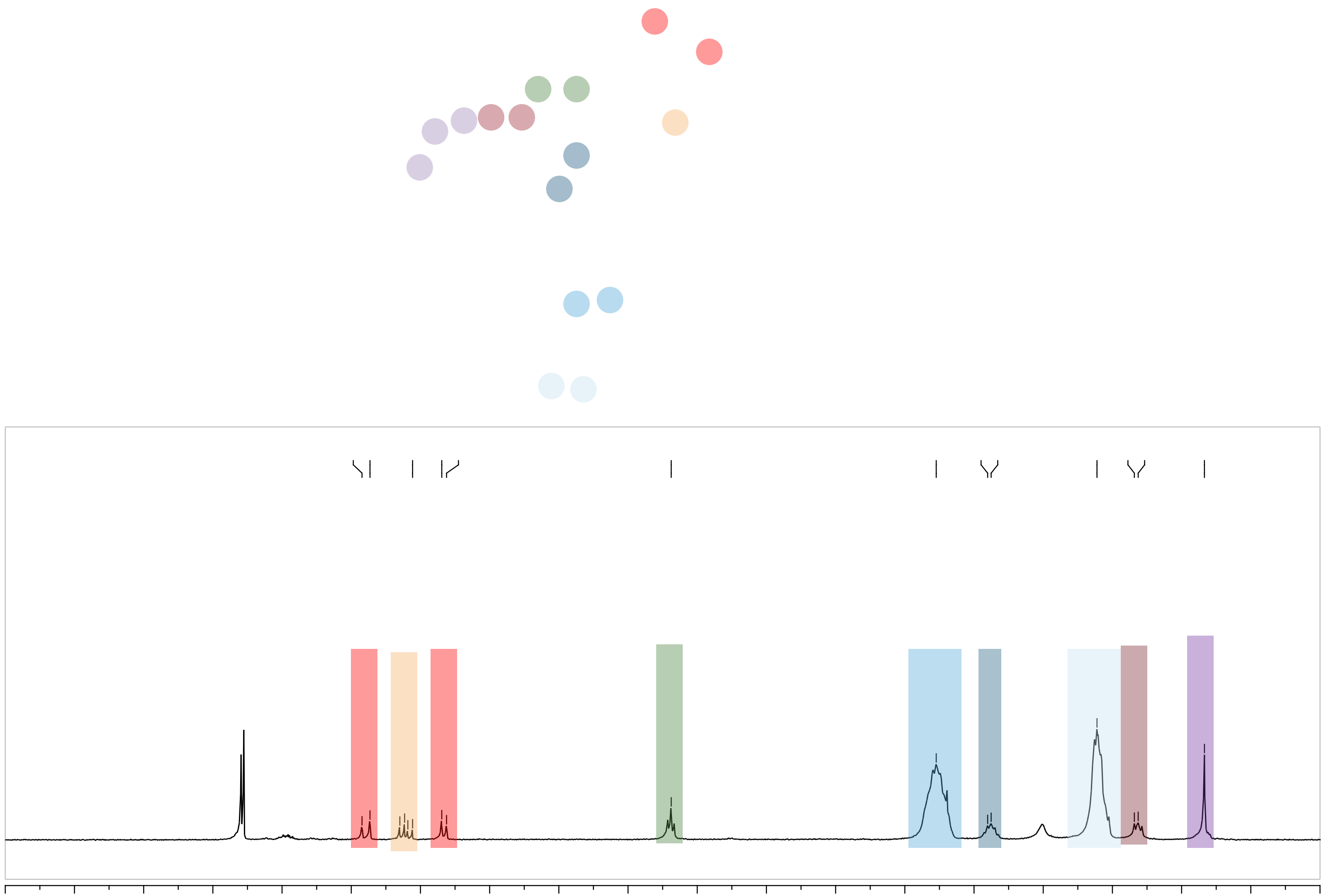
$R_1 = CH_3$
$R_2 = CH_2CH_2CH_2\ OC(O)CHCH_2$



^{29}Si NMR taken in fluorinated solvent

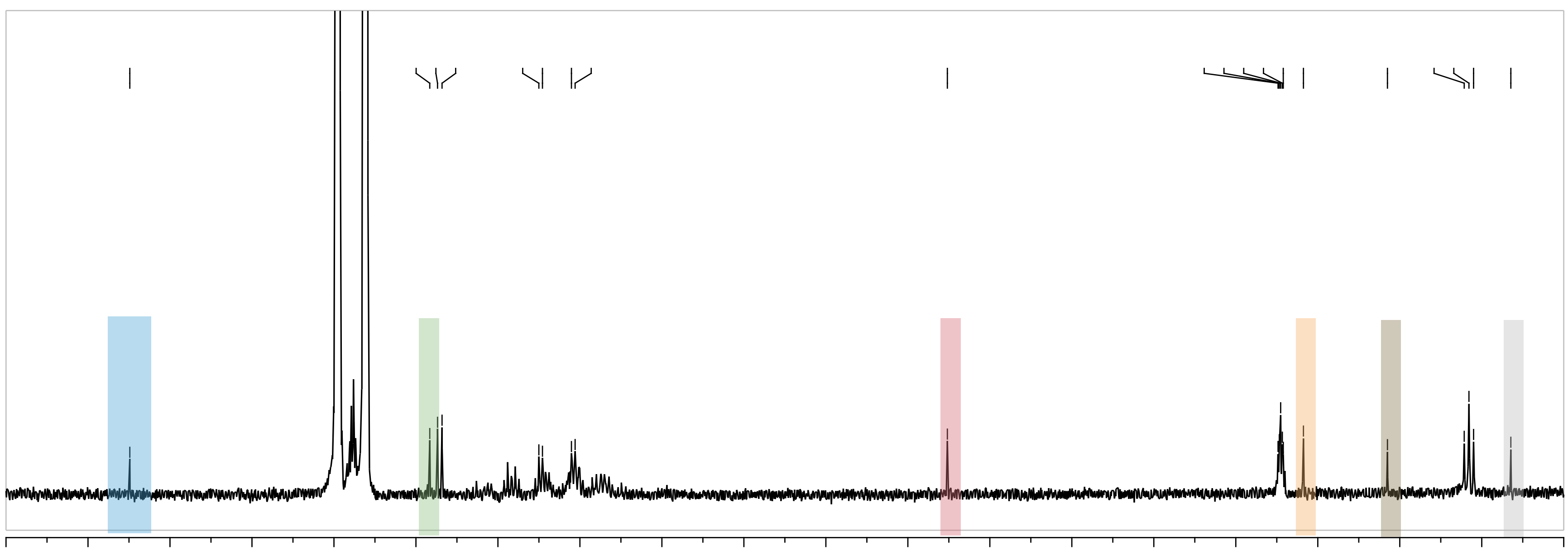
- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**

^{1}H NMR Characterization of Compounds



^{19}F NMR taken in diethyl ether. ^{1}H NMR taken in $C_6F_6/CDCl_3$ mixture.

^{13}C NMR Characterization of Compounds



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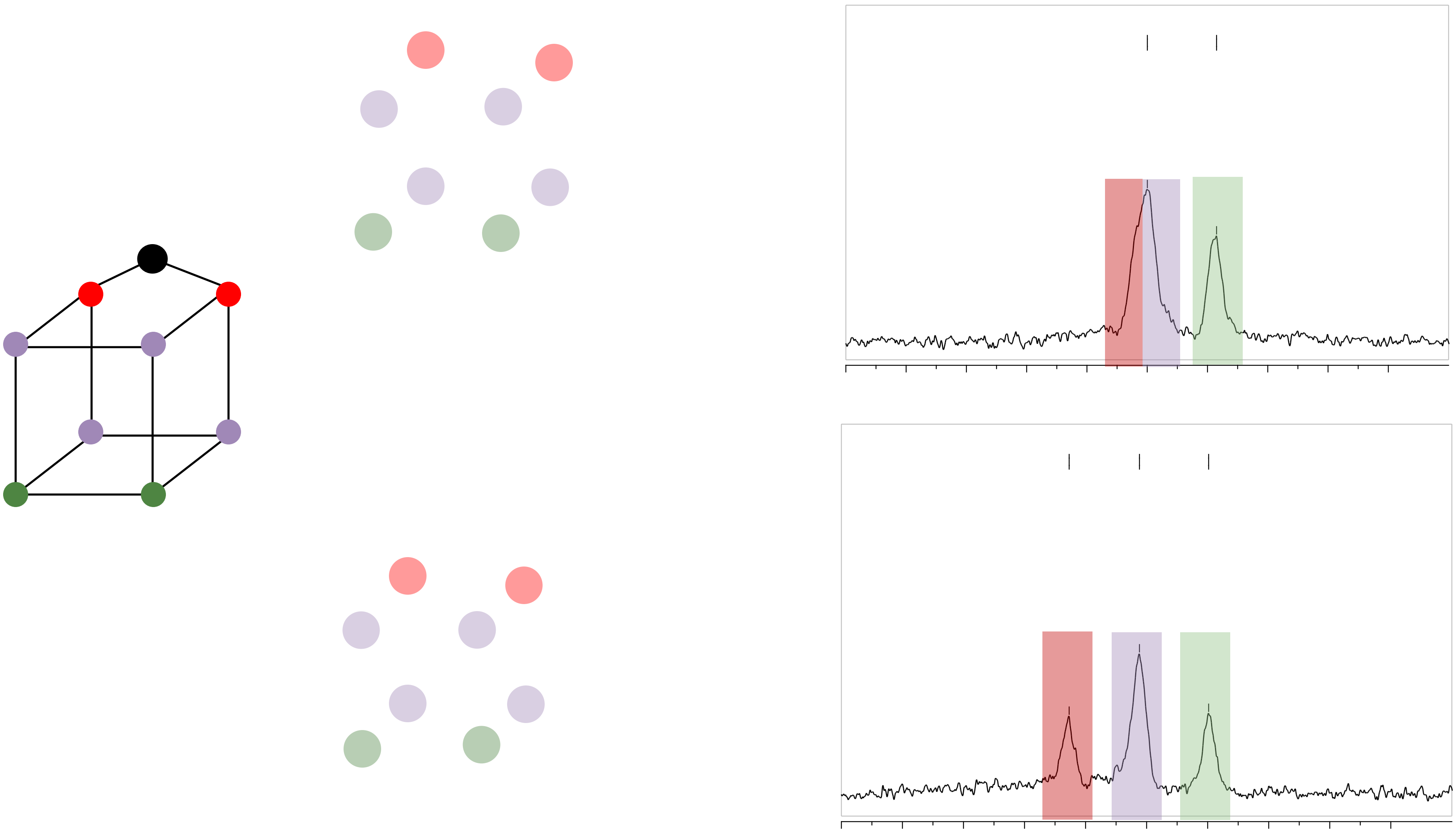

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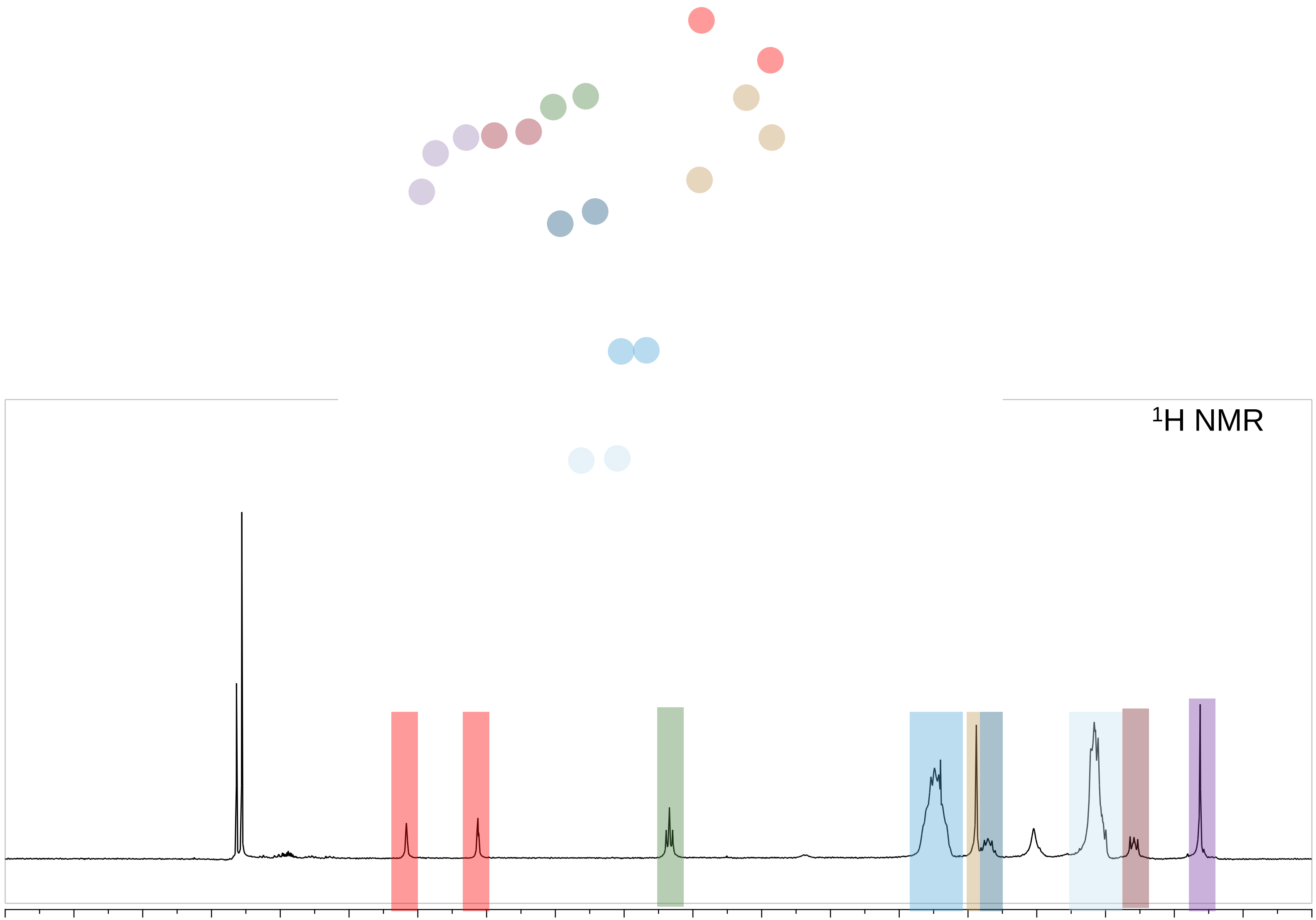
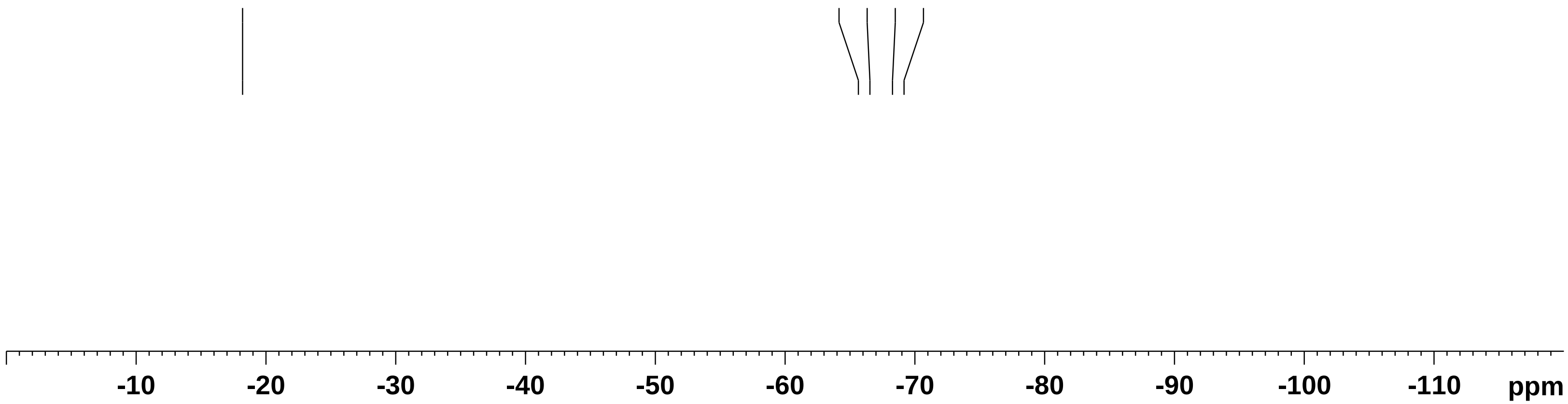


^{19}F NMR taken in diethyl ether. ^{1}H NMR taken in $C_6F_6/CDCl_3$ mixture.

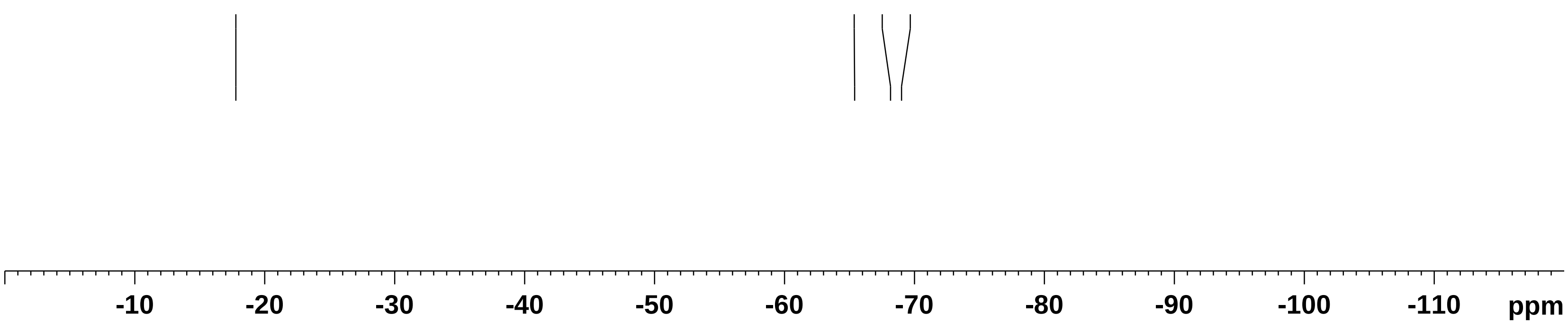
Separation of T_8 from Product

Before



^{29}Si NMR taken in fluorinated solvent

After



^{29}Si NMR taken in **diethyl ether-d$_{10}$**

F-POSS Structures Synthesized

-29.5 ppm

-17.8ppm

-32.1 ppm

-17.8 ppm

-45.5 ppm

-17.1 ppm

-17.9 ppm

R = $CH_2CH_2(CF_2)_7CF_3$

Contact Angle Measurements

- Non-wetting surfaces can be developed by a combination of three parameters
  - Chemical functionality (high fluorine content)
  - Roughness (micro- and nanoscale)
  - Surface Geometry (re-entrant curvature)
- *What type of influence will functional groups have on F-POSS surface properties?*
- *Solvent impact?*

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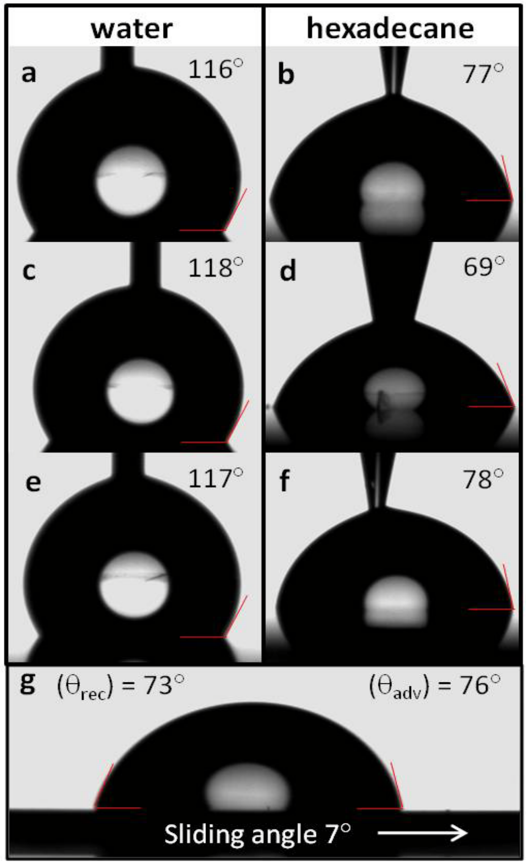
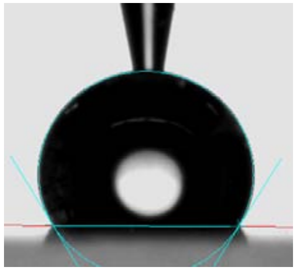


Static contact angles of Si wafer surfaces coated with compounds **disilanol** (a) and (b), **dioctyl** (c) and (d), and **diphenyl** (e) and (f). Image of hexadecane droplet (10μL) rolling off surface coated with compound **diphenyl** (g).

Contact Angle Measurements



Functional Group on F-POSS	water		hexadecane	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	124 ± 0.5°	109.6 ± 0.7°	79.1 ± 0.4°	65.1 ± 0.5°
$Si\text{-}(OH)_2$	116.8 ± 0.4°	111 ± 0.6°	77.4 ± 0.4°	74.4 ± 0.8°
$Si\text{-}(CH_3)(CH{=}CH_2)$	116.2 ± 0.4°	100.6 ± 0.8°	78.4 ± 0.3°	70.6 ± 2.3°
$Si((CH_3)((CH_2)_3OC(O)CCH{=}CH_2)$	118.2 ± 1.0°	90.6 ± 1.0°	76.8 ± 0.3°	64.8 ± 1.0°
$Si\text{-}(CH_3)(\,(CH_2)_3OC(O)C(CH_3){=}CH_2)$	117.1 ± 0.6°	93.8 ± 1.5°	78.1 ± 0.4°	63.0 ± 1.2°
$Si\text{-}(CH_3)((CH_2)_{22}CH_3)$	117.9 ± 0.4°	96.9 ± 1.9°	78.0 ± 0.4°	16.2 ± 5.5°
$Si\text{-}(C_6H_5)_2$	116.2 ± 0.4°	110.5 ± 0.5°	76.0 ± 0.8°	73.2 ± 0.4°
$Si\text{-}((CH_2)_7CH_3)_2$	117.9 ± 0.5°	95.5 ± 0.4°	69.1 ± 1.2°	23.1 ± 1.2°

Samples (10 mg/mL) were spin casted on oxygen-plasma cleaned Si wafers at 900 rpm for 30 seconds. Contact angle measurements were run in triplicate. Surface roughness < 5nm (AFM and Optical Profilometry).

*Chhatre, S. S.; Guardado, J. O.; Moore, B. M.; Haddad, T. S.; Mabry, J. M.; McKinley, G. H.; Cohen, R. E. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3544.

Copolymerizations

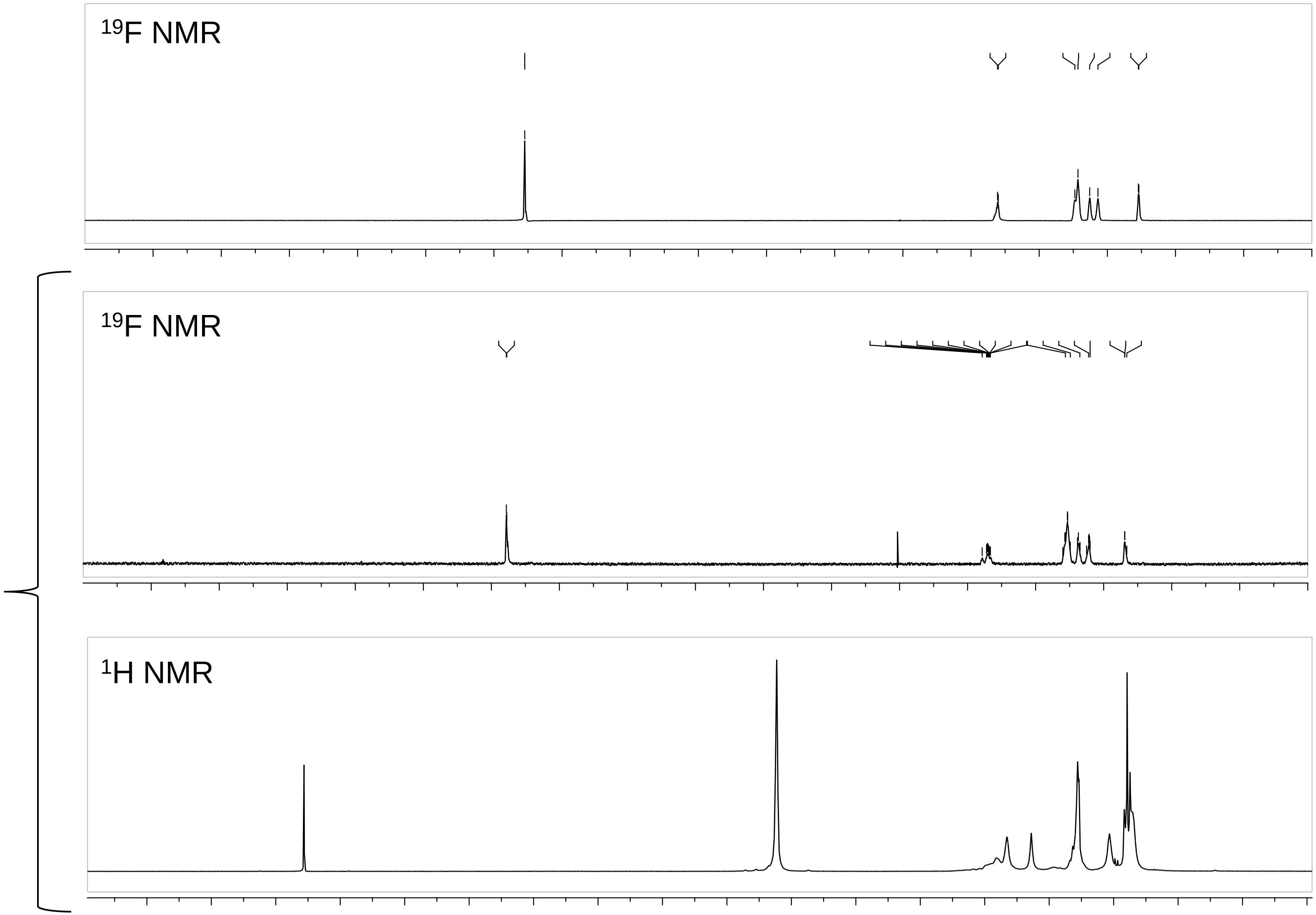
MMA
(MW = 100 g/mol)

MMA-F-POSS
(MW = 4178 g/mol)

	Weight (g)		***Weight***	***Monomer (mmol)***		***Mol Ratio***	***Initator***	***Conversion***
	MMA-F-POSS	***MMA***	***(%)***	***MMA-F-POSS***	***MMA***	***(MMA:MMA-F-POSS)***	***(mol %)***	***(%)***
SR-3-141	0.085	1.311	6.3	0.02	13.1	655	0.5	42
SR-3-145	0.362	1.31	21.6	0.09	13.1	145	0.2	71

Sampe 141 was run in pure C_6F_6.
Sample 145 was run in a THF/C_6F_6 mixture.

NMR Characterization of Copolymers



Future Directions

- Surface Functionalization

276 - FluoroPOSS monolayers covalently bound to a silica surface
Authors: Raymond Campos, Dr. Sean M Ramirez PhD, Dr. Timothy S Haddad PhD, Dr. Joseph M Mabry PhD
Division: POLY: Division of Polymer Chemistry
Date/Time: Tuesday, March 29, 2011 - 02:30 PM
Session Info: POLY/PMSE Poster Session (02:30 PM - 04:00 PM)
Location: Hilton Anaheim
Room: California Blrm D

- Polymerizations of monomers

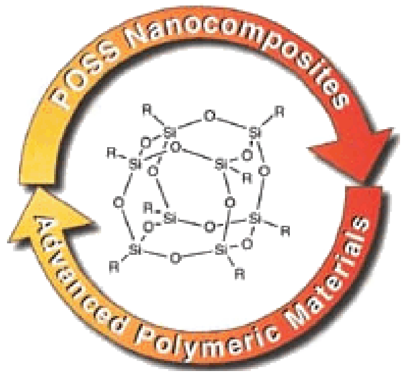
Summary

- Synthesis of disilanol F-POSS from F-POSS was accomplished in a three step reaction process
- Structures were demonstrated to be reactive towards a variety of dichlorosilanes
- Solubility of F-POSS compounds were shown to be influenced by chemical functionality
- Functionality was shown to be influential on contact angle measurements
- F-POSS compounds have a near limitless potential in producing a variety of new hydrophobic, oleophobic, or ominiphobic polymer composites.
  - Reaction mechanisms, polymer composites, block copolymers, etc….

Polymer Working Group

The Polymer Working Group at Edwards Air Force Base:

Dr. Joseph Mabry
Mr. Ray Campos
Mr. Pat Ruth
Ms. Vandana Vij
Dr. Greg Yandek
Ms. Sarah Weber



Mr. Brian Moore
Dr. Joe Mabry
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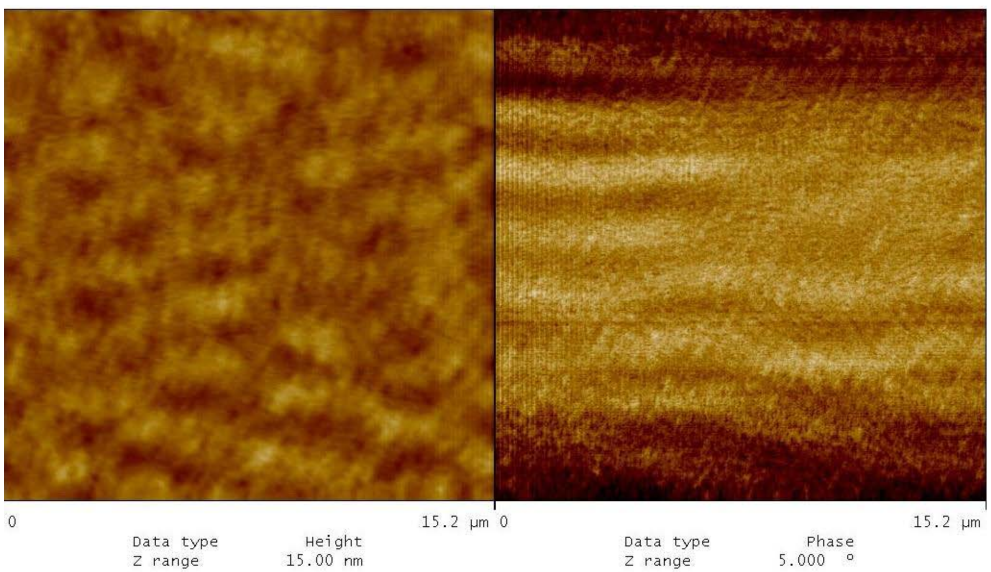
Dr. Tim Haddad
Lt Becky Stone
Dr. Andy Guenthner

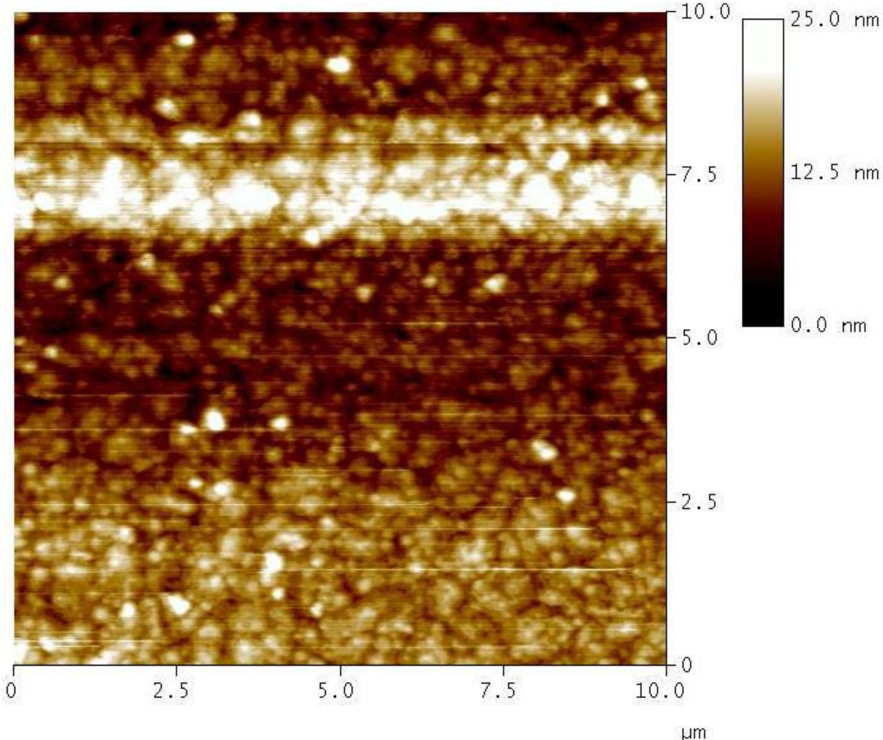
Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

Optical Profilometry and (AFM) Measurements

- Diol – R_a = 1.59 nm (3.88 nm)
- Vinyl – R_a = 1.25 nm (1.22 nm)
- Acrylate - R_a = 0.84 nm (1.83 nm)
- Methacylate – R_a = 2.85 nm (0.85 nm)

Acrylate





Diol

Raw AFM images shown